

## DESCRIPTION

IRON OXIDE POWDER FOR UNDERCOAT LAYER OF COAT-TYPE MAGNETIC  
RECORDING MEDIUM HAVING MULTILAYER STRUCTURE AND A PROCESS  
5 OF PRODUCING THE SAME

### Technical Filed

This invention relates to a magnetic iron oxide powder containing cobalt which can be used to form an undercoat layer of a coat-type magnetic recording medium having a multilayer structure.

10 As the recording density of coat-type magnetic recording media increases (i.e., as the recording wavelength is shortened), a magnetic domain as the smallest unit of recording becomes smaller. With the resultant reduction of the magnetic domain size (length in the magnetization direction) to magnetic layer thickness ratio, a demagnetization field increases to increase the self-demagnetization loss. To solve this  
15 problem it is necessary to reduce the magnetic layer thickness with respect to the magnetic domains. However, a magnetic layer of 2  $\mu\text{m}$  or thinner directly formed on a substrate is susceptible to the influences of the non-magnetic substrate, tending to suffer from deterioration of electromagnetic characteristics, dropouts, and the like. To address this problem, JP-A-5-182178 proposes a magnetic recording medium having a multilayer  
20 structure composed of a substrate, a non-magnetic undercoat layer comprising inorganic powder dispersed in a binder, and a magnetic layer comprising ferromagnetic powder dispersed in a binder and having a thickness of 1.0  $\mu\text{m}$  or smaller which is formed on the undercoat layer while the undercoat layer is wet. Magnetic tapes composed of such a thin magnetic layer and such a non-magnetic undercoat layer have been put to practice use  
25 as DTL IV or DDS-4 format tapes for high-density high-capacity computer systems. Nevertheless the demands for magnetic recording media such as discs and tapes with further increased capacity and density have been still growing without bounds, requiring further improvements on performance characteristics.

In the coat-type magnetic recording media having the multilayer structure, the

surface smoothness of the undercoat layer is an important requirement. JP-A-9-170003, JP-A-10-198948, and JP-A-10-273325 report attempts to improve dispersibility of iron oxide powder for the undercoat layer. However, an iron oxide powder which has enough dispersibility to form an undercoat layer with a smooth surface has not been available as yet.

A tape end detection system utilizing transmitted light is currently adopted for implementing auto-shutoff or autoreverse at the end of tape. This system detects a difference in transmitted light intensity between an area coated with both the upper magnetic layer and the lower undercoat layer and a non-coated area. However, the particles constituting the coated area are smaller in size than optical wavelengths and transparent to show an extremely small difference in light transmittance from the non-coated area, resulting in a failure of tape end detection. Besides, because such fine particles are electrically insulating, a tape containing the same ought to have a high resistance and will be electrostatically charged by the friction with a head on running. Therefore, it has been necessary to add increased amounts of a low light transmittance material and a high conductivity material or a material having low light transmittance and high conductivity.

#### Disclosure of the Invention

An object of the present invention is to provide a magnetic iron oxide powder for forming an undercoat layer of a coat-type magnetic recording medium having a multilayer structure which has excellent dispersibility, capability of forming a smooth undercoat layer, low light transmittance, and high electrical conductivity, and a process of producing the powder.

The above object is accomplished by an iron oxide powder for an undercoat layer of a coat-type magnetic recording medium having a multilayer structure which comprises cobalt-doped iron oxide particles having an average length of 0.02 to 0.3  $\mu\text{m}$ , an aspect ratio (length to width ratio) of 2 to 13, and a BET specific surface area of 40 to 100  $\text{m}^2/\text{g}$  and containing a cobalt compound in an amount of 0.2 to 10 atom% in terms of cobalt based on total iron.

The above object is also accomplished by a process of producing iron oxide

powder for an undercoat layer of a coat-type magnetic recording medium having a multilayer structure, which comprises the steps of synthesizing goethite, filtering the resulting goethite slurry, washing the filter cake with water, drying the cake, and firing the resulting goethite powder at 400 to 600°C, wherein an aqueous cobalt salt solution is added to the system of synthesizing goethite when 50 to 100% of iron (II) is oxidized to iron (III) in the step of synthesizing goethite, followed by continuation of the oxidation reaction to produce cobalt-doped iron oxide particles having an average length of 0.02 to 0.3  $\mu\text{m}$ , an aspect ratio (length to width ratio) of 2 to 13, and a BET specific surface area of 40 to 100  $\text{m}^2/\text{g}$  and containing a cobalt compound in an amount of 0.2 to 10 atom% in terms of cobalt based on total iron.

#### Best Mode for Carrying out the Invention

The iron oxide powder for undercoat layer according to the present invention comprises cobalt-doped iron oxide particles. The cobalt-doped iron oxide particles internally contain 0.2 to 10 atom%, preferably 0.5 to 8.5 atom%, in terms of cobalt, of a cobalt compound based on the total iron. The iron oxide powder of the present invention exhibits higher dispersibility than conventional non-magnetic iron oxide powders for undercoat layer by virtue of its cobalt content. With a cobalt content less than 0.2 atom% or more than 10 atom%, the powder fails to exhibit required optical absorption, namely, has a high light transmittance. The powder having high light transmittance gives only a small difference in transmitted light intensity between a coated area and a non-coated area in magnetic tapes, which makes tape end detection difficult.

The presence of 0.2 atom% or more of cobalt based on total iron makes the iron oxide powder highly conductive. With a cobalt content less than 0.2 atom%, the conductivity is low, which results in high electric resistance of magnetic recording medium, to fail to prevent the magnetic recording medium from being triboelectrically charged due to slide running on a head. As a result, the recording medium is apt to attract dust, etc., leading to increased dropouts.

The cobalt compound includes cobalt chloride, cobalt sulfate, and cobalt nitrate.

The cobalt-doped iron oxide particles have an average length of 0.02 to 0.3  $\mu\text{m}$ , preferably 0.05 to 0.25  $\mu\text{m}$ . Particles with an average particle length smaller than

0.02  $\mu\text{m}$  are difficult to disperse in a vehicle due to the increased force of aggregation. Particles longer than 0.3  $\mu\text{m}$  are too large to assure surface smoothness of the undercoat layer.

The cobalt-doped iron oxide particles are acicular particles having an aspect ratio (length to width ratio) of 2 to 13, preferably 4 to 11. If the aspect ratio is smaller than 2, the particles have reduced structural viscosity in a disperse system, which is generally attributed to the particle shape, and are difficult to harmonize with a magnetic coating used to form an upper magnetic layer. Further, particles having an aspect ratio smaller than 2 undergo little effect of compression in calendaring after coating and drying for creating a mirror finish. If the aspect ratio exceeds 13, such elongated particles are easily entangled with each other or broken when dispersed only to give a coating of poor particle size distribution.

The cobalt-doped iron oxide particles have a BET specific surface area of 40 to 100  $\text{m}^2/\text{g}$ , preferably 45 to 65  $\text{m}^2/\text{g}$ . Particles having a BET specific surface area less than 40  $\text{m}^2/\text{g}$  are so large as to spoil the surface smoothness of the undercoat layer. Particles with a BET specific surface area more than 100  $\text{m}^2/\text{g}$  are difficult to disperse in a vehicle, resulting in a failure to provide a smooth surface.

The cobalt-doped iron oxide powder is preferably cobalt-doped  $\alpha$ -iron oxide powder. It is preferred for the cobalt-doped iron oxide powder to have a coercive force of 15 to 60 kA/m, particularly 20 to 50 kA/m, and a saturation magnetization of 0.2 to 5.0  $\text{Am}^2/\text{kg}$ , particularly 0.25 to 2.0  $\text{Am}^2/\text{kg}$ .

The iron oxide particles having a coercive force and a saturation magnetization in the above respective ranges are oriented when an undercoat layer is applied and oriented or when an undercoat layer and an upper magnetic layer are applied simultaneously, thereby assuring smoothness of the undercoat layer surface. Iron oxide particles having a coercive force less than 15 kA/m or a saturation magnetization less than 0.2  $\text{Am}^2/\text{kg}$  are hardly oriented as conventional non-magnetic iron oxide powders even where an undercoat layer is applied and oriented or where an undercoat layer and an upper magnetic layer are applied simultaneously, making no more contribution to undercoat layer surface smoothness. If the iron oxide particles have a coercive force greater than 60 kA/m or a

saturation magnetization greater than  $5.0 \text{ Am}^2/\text{kg}$ , an undercoat layer formed of such particles will participate in magnetic recording and accelerate self-demagnetization loss or cause noise.

5 The Co-doped iron oxide particles may contain salts of metals, e.g., nickel, iron and aluminum, for the purpose of controlling crystallinity, improving particle size distribution, increasing aspect ratio, improving shape retention on firing, preventing fusion between particles, and improving dispersibility.

10 The iron oxide powder for forming an undercoat layer which comprises the above-described cobalt-doped iron oxide powder can be produced by adding an aqueous cobalt salt solution to a goethite synthesis system in the course of oxidation (after 50 to 100% of iron (II) is oxidized to iron (III), preferably after 75% of iron (II) has been oxidized and by the time when 90% of iron (II) has been oxidized) to co-precipitate cobalt, followed by continuation of the oxidation reaction, and treating the resulting goethite slurry by filtration, washing with water, drying, and firing.

15 Goethite can be synthesized by neutralizing a ferrous salt aqueous solution which, if necessary, contains a ferric salt or other metal salts, e.g., a nickel salt and a zinc salt, by mixing with at least a stoichiometrically requisite amount of an alkali or an alkali carbonate and oxidizing the resulting ferrous hydroxide by bubbling an oxygen-containing gas (such as air) through the system.

20 The concentration of the aqueous ferrous salt solution is usually 0.02 to 2 mol/l, preferably 0.05 to 2 mol/l, still preferably 0.1 to 0.8 mol/l. In concentrations higher than 0.8 mol/l, stirring would be insufficient because of high viscosity so that the resulting dispersion tends to be non-uniform. Solutions in concentrations higher than 2 mol/l are difficult to stir. Solutions in concentrations lower than 0.02 mol/l are disadvantageous  
25 for industrial productivity.

The alkali to be added includes sodium hydroxide, potassium hydroxide, and ammonia. The alkali carbonate includes sodium carbonate, sodium hydrogencarbonate, ammonium carbonate, and ammonium hydrogencarbonate.

The alkali is added in an equivalent or more amount, preferably in amounts up to five equivalents. From the standpoint of particle distribution and independence of individual particles, alkali carbonates are preferred. The alkali carbonate is added in an equimolar or more amount, preferably 1.5 to 3.0 equivalents, to iron. Use of more than 3 equivalents of an alkali carbonate, being expensive, results in an increased cost, which is industrially disadvantageous for performance. Other metal salts, such as nickel, zinc or aluminum salts, may be added for the purpose of controlling crystallinity, improving particle size distribution, increasing the aspect ratio, and the like.

The oxidation with an oxidizing gas, such as air or oxygen gas, is usually carried out at 20 to 90°C, preferably 30 to 70°C. Oxidation at temperatures higher than 70°C can result in formation of magnetite in addition to goethite. An advisable upper temperature limit is 90°C. Oxidation at temperatures lower than 30°C not only needs too much time, which is industrially inefficient, but can result in formation of plate-like products and amorphous (low-crystallinity) particles. An advisable lower temperature limit is 20°C.

An aqueous cobalt salt solution is added to the goethite synthesis system in the course of the oxidation reaction to co-precipitate cobalt. After the addition, the oxidation reaction is continued to obtain a cobalt-doped goethite slurry. The cobalt salt includes cobalt chloride, cobalt sulfate, and cobalt nitrate.

The resulting cobalt-doped goethite slurry is filtered, and the filter cake is washed with water, dried at 100 to 200°C for 8 to 20 hours, and fired at 400 to 600°C to obtain a black cobalt-doped iron oxide powder according to the invention.

When fired at temperatures higher than 600°C, the particles undergo deformation or agglomeration due to sintering between particles. Where the particles are fired at temperatures lower than 400°C, the resulting cobalt-doped iron oxide particles will have a large number of pores and a low degree of crystallinity. Such particles are brittle and easily broken when formulated into a coating composition. A preferred firing temperature is from 450 to 550°C, and a preferred firing time is 1 to 5 hours, particularly 2 to 3 hours.

For improving shape retention on firing, preventing agglomeration on firing, and

improving dispersibility, the cobalt-doped iron oxide particles can be coated with an appropriate amount of aluminum, silica, etc. by co-precipitation or coating.

The present invention will now be illustrated in greater detail with reference to Examples in view of Comparative Examples, but it should be understood that the present invention is not construed as being limited thereto.

The characteristics of iron oxide powders for undercoat layer formation and of undercoat layers shown in Examples and Comparative Examples were measured as follows.

1) Shape of iron oxide particles

A transmission electron micrograph (x30000) taken of an iron oxide powder was enlarged four times, and the lengths of the major axis and the minor axis of arbitrarily selected 200 particles were measured to obtain respective averages.

2) BET specific surface area of iron oxide particles

Measured by the BET method with Tetrasorb 4-Sample Automatic Surface Area Analyzer 4SU2, supplied by Yuasa-Ironics Co., Ltd.

3) Magnetic characteristics of iron oxide powder

An iron oxide powder was lightly ground in a mortar, and its magnetic characteristics in a magnetic field of 10 kOe were measured with a vibrating-sample magnetometer (BHV-30, supplied from Riken Denshi Co., Ltd.).

4) Specific resistance of iron oxide powder

An iron oxide powder was press molded into a disc of 13 mm in diameter and 2 mm in thickness. The disc held in between a pair of electrodes, 1V voltage applied, and the resistivity was measured.

5) Viscosity of coating composition for undercoat layer

The viscosity of a coating composition prepared was measured at 25°C with a Haake Rotovisco viscometer (model RV-12) equipped with a rotor MV-DIN at 32 rpm.

6) Gloss of undercoat layer (dispersion stability of coating composition)

A 60° gloss of an undercoat layer was measured with Handy Glossmeter PG-1 available from Nippon Denshoku Industries Co., Ltd. Dispersion stability of a coating composition was evaluated by a change (%) from the gloss of an undercoat layer formed of a coating composition immediately after preparation and that of an undercoat layer formed of the same coating composition after standing for 60 minutes from the preparation. A smaller change of gloss indicates higher dispersion stability of the coating composition.

7) Surface roughness Ra of undercoat layer

An average center-line roughness (Ra) of an undercoat layer was measured with Surfcom 575A.

8) Light transmittance of undercoat layer

Light transmittance of a dried coating film applied to a 25 μm thick polyester film were measured in the visible region and at 900 nm, using the uncoated polyester film as a blank.

### EXAMPLE 1

A reactor equipped with a stirrer and a gas introducing tube was purged with nitrogen gas to expel oxidizing gas. An alkali solution of 18 mol of sodium carbonate and 6 mol of sodium hydroxide in 40 l of pure water was put into the reactor. A solution of 12 mol of ferrous chloride in 20 l of pure water was mixed into the alkali solution to prepare a suspension. The suspension was kept at 50°C for 1 hour and then oxidized with 2.0 l/min of air for 2 hours. A solution of 0.6 mol of cobalt chloride in 5.0 l of pure water was added to the reaction mixture, and the oxidation was continued to oxidize iron (II) to iron (III). The reaction mixture was filtered, and the filter cake was washed with water and dried in a dryer at 140°C for 10 hours to obtain about 1.1 kg of a cobalt-doped goethite cake. The cake was fired at 500°C for 2 hours in air to obtain about 1.0 kg of a cobalt-doped iron oxide powder.

### EXAMPLE 2

A cobalt-doped iron oxide powder was obtained in the same manner as in Example



1, except for changing the amount of cobalt chloride to 0.06 mol.

### EXAMPLE 3

5 A cobalt-doped iron oxide powder was obtained in the same manner as in Example 1, except for changing the amount of cobalt chloride to 0.12 mol.

### EXAMPLE 4

A cobalt-doped iron oxide powder was obtained in the same manner as in Example 1, except for changing the amount of cobalt chloride to 1.0 mol.

### EXAMPLE 5

10 A cobalt-doped iron oxide powder was obtained in the same manner as in Example 1, except for using a solution of 24 mol of ammonium carbonate in 40 l of 1.8 mol/l aqueous ammonia as an alkali solution.

### EXAMPLE 6

15 A cobalt-doped iron oxide powder was obtained in the same manner as in Example 1, except for using a solution of 60 mol of sodium hydroxide in 40 l of pure water as an alkali solution.

### COMPARATIVE EXAMPLE 1

An iron oxide powder was obtained in the same manner as in Example 1, except that an aqueous cobalt chloride solution was not added.

### 20 COMPARATIVE EXAMPLE 2

An iron oxide powder was obtained in the same manner as in Example 5, except that an aqueous cobalt chloride solution was not added.

### COMPARATIVE EXAMPLE 3

An iron oxide powder was obtained in the same manner as in Example 6, except

that an aqueous cobalt chloride solution was not added.

#### COMPARATIVE EXAMPLE 4

A cobalt-doped iron oxide powder was obtained in the same manner as in Example 1, except for changing the amount of cobalt chloride to 2.0 mol.

- 5        The characteristics of the iron oxide powders (cobalt-doped or non-doped) prepared in Examples 1 to 6 and Comparative Examples 1 to 4 are shown in Table 1 below.

TABLE 1

	Co Content (atom%/Fe)	Shape of Particles			BET Specific Surface Area (m <sup>2</sup> /g)	Coercive Force (kA/m)	$\sigma_r$ (Am <sup>2</sup> /kg)	$\sigma_s$ (Am <sup>2</sup> /kg)	$\sigma_r/\sigma_s$	Disc	
		Length ( $\mu$ m)	Width ( $\mu$ m)	Aspect Ratio						Specific Resistance ( $\Omega$ -cm)	Density (g/cm <sup>3</sup> )
Ex. 1	5.0	0.13	0.028	4.6	56.8	37.4	0.38	1.50	0.250	$4.5 \times 10^5$	1.68
Ex. 2	0.5	0.14	0.025	5.6	56.6	20.7	0.03	0.20	0.190	$9.5 \times 10^5$	1.65
Ex. 3	1.0	0.14	0.028	5.0	58.2	27.1	0.09	0.40	0.220	$5.0 \times 10^5$	1.65
Ex. 4	8.3	0.12	0.026	4.6	57.2	46.2	0.45	1.65	0.270	$1.0 \times 10^5$	1.65
Ex. 5	5.0	0.13	0.028	4.6	57.8	33.4	0.42	1.60	0.260	$4.8 \times 10^6$	1.68
Ex. 6	5.0	0.28	0.028	11.0	57.1	31.8	0.38	1.52	0.250	$5.0 \times 10^5$	1.68
Comp. Ex. 1	0	0.14	0.025	5.6	57.6	14.9	0.03	0.15	0.170	$1.8 \times 10^7$	1.65
Comp. Ex. 2	0	0.14	0.025	5.6	55.9	14.5	0.03	0.15	0.175	$3.5 \times 10^7$	1.69
Comp. Ex. 3	0	0.28	0.026	10.8	54.1	14.7	0.02	0.14	0.170	$2.6 \times 10^7$	1.65
Comp. Ex. 4	16.7	0.14	0.028	5.0	56.5	65.3	0.54	1.80	0.300	$9.0 \times 10^4$	1.67

## EXAMPLES 7 TO 12 AND COMPARATIVE EXAMPLES 5 TO 8

Each of the iron oxide powders of Examples 1 to 6 and Comparative Examples 1 to 4 was compounded into a coating composition according to the formulation shown below.

The resulting coating composition was applied to a polyester base film to form an undercoat layer. The characteristics of the undercoat layer are shown in Table 2.

## Undercoating layer formulation:

Iron oxide powder 100 parts (by weight, hereinafter the same)

Vinyl chloride-vinyl acetate copolymer (MR-110, available from Zeon Corp.)  
15 parts

Urethane resin (UR-8200, available from Toyobo Co. Ltd.) 15 parts

Toluene 135 parts

Methyl ethyl ketone 135 parts

Cyclohexanone 120 parts

TABLE 2

	Iron Oxide Powder	Co Content (atom%/Fe)	Coating Composition Viscosity (cP)	Coating Thickness ( $\mu\text{m}$ )	Ra (nm)	Gloss (%)	Dispersion Stability (Gloss Change) (%)	Light transmittance (%)	
								Visible Light	900 nm
Ex. 7	Ex. 1	5.0	270	2.8	5.8	250	0.5	1.1	5.8
Ex. 8	Ex. 2	0.5	258	2.8	12.8	160	5.7	16.2	42.8
Ex. 9	Ex. 3	1.0	294	2.8	6.3	220	2.6	3.8	15.0
Ex. 10	Ex. 4	8.3	252	2.8	5.9	170	8.8	17.5	39.9
Ex. 11	Ex. 5	5.0	300	2.8	5.1	220	0.7	4.5	15.0
Ex. 12	Ex. 6	5.0	432	2.8	7.2	280	0.9	4.5	15.0
Comp. Ex. 5	Comp. Ex. 1	0	324	2.8	32.7	130	18.5	21.2	58.8
Comp. Ex. 6	Comp. Ex. 2	0	318	2.8	42.9	100	14.2	23.8	60.4
Comp. Ex. 7	Comp. Ex. 3	0	444	2.8	60.6	120	13.9	24.8	56.7
Comp. Ex. 8	Comp. Ex. 4	16.7	246	2.8	5.9	165	8.8	25.1	63.9

## EXAMPLES 13 TO 18 AND COMPARATIVE EXAMPLES 9 TO 12

An undercoat layer was formed on a polyester base film in the same manner as in Examples 7 to 12 and Comparative Examples 5 to 8, except that the applied coating was subjected to orientation in a magnetic field of 1600 G. The characteristics of the resulting undercoat layer are shown in Table 3.

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TABLE 3

	Iron Oxide Powder	Ra (nm)	Gloss (%)	Dispersion Stability (Gloss Change) (%)	Light transmittance (%)	
					Visible Light	900 nm
Example 13	Example 1	4.8	290	0.4	1.0	5.3
Example 14	Example 2	11.9	178	5.4	14.6	38.6
Example 15	Example 3	5.9	230	2.5	3.4	13.5
Example 16	Example 4	5.1	180	8.1	15.8	35.9
Example 17	Example 5	4.7	240	0.2	4.1	13.5
Example 18	Example 6	6.8	310	0.3	4.1	13.2
Compara. Example 9	Compara. Example 1	33.1	130	19.0	21.1	58.2
Compara. Example 10	Compara. Example 2	42.8	100	14.5	22.7	60.1
Compara. Example 11	Compara. Example 3	58.8	120	13.8	24.0	56.4
Compara. Example 12	Compara. Example 4	5.1	170	7.9	24.3	62.8

The iron oxide powder according to the present invention has a low light transmittance, high conductivity, and excellent dispersibility and is therefore capable of forming a satisfactory undercoat layer for a coat-type magnetic recording medium having a multilayer structure. When the iron oxide powder comprising cobalt-doped iron oxide particles having a coercive force of 15 to 60 kA/m and a saturation magnetization of 0.2 to 5.0 Am<sup>2</sup>/kg is applied and oriented to form an undercoat layer or applied simultaneously with an upper magnetic layer, the particles are oriented to form an undercoat layer with a smoother surface.